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✓ Spreadsheet
✓ DTS

MEMORANDUM FOR PRR (~~Contractor~~/In-House Publication)

1 June 1999

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Fajardo, "Cryosolid Propellants – The Last "Revolutionary" HEDM Concept"

Presentation HEDM CONFERENCE

(Public Release)

HIGH ENERGY DENSITY MATTER CONTRACTORS CONFERENCE
Cocoa Beach, FL 8-11 June 1999

Cryosolid Propellants The Last "Revolutionary" HEDM Concept

Mario E. Fajardo
US Air Force Research Laboratory, Propulsion Directorate
(AFRL/PRSP Bldg. 8451, Edwards AFB, CA 93524-7680)
mario_fajardo@ple.af.mil

Introduction

"Revolutionary" vs. "Evolutionary" HEDMs
HEDM Cryosolid Propellants

AFRL/Edwards Experimental Effort

- HEDM Dopant Source Development
- Dopant Source Characterization
- Cryosolids Characterization
  (thick, concentrated samples)

Summary

“Revolutionary” vs. “Evolutionary” HEDM

“Revolutionary” means better than LOX/LH_2

LOX/LH_2	$\Delta H_{sp} = 12.6$ MJ/kg (3.0 kcal/g)
HEDM Target:	$\Delta H_{sp} > 15.0$ MJ/kg (3.6 kcal/g)

Early (c1990) Revolutionary HEDM Concepts:

- tetrahydrogen (H_4)
- metastable triplet helium (He^* and He_2^*)
- spin-polarized atomic hydrogen ($H\uparrow$)
- high-spin species (^5CO)
- dications (AB^{++}, ABC^{++})
- “non-metallics” (*e.g.*, O_4/H_2, N_4, N_8, N_{20})
- metallic hydrogen
- metal atoms and clusters in solid H_2

HEDM Cryosolid Propellants Objectives

- Trap 5% molar concentration of energetic additives in solid hydrogen.

- Demonstrate size-scaleable sample production method.

HEDM Cryosolid Propellants Payoffs

Increased Specific Impulse

$I_{sp} \propto \sqrt{\Delta H_{sp}}$

$LOX/LH_2 : I_{sp} = 390$ s

5% $B/sH_2 + LOX : I_{sp} = 500$ s (+30%)* 350 → 650

* calculated for $P_{chamber} = 1000$ psia ~~PSIA~~, $P_{exhaust} = 14.7$ psia ~~PSIA~~

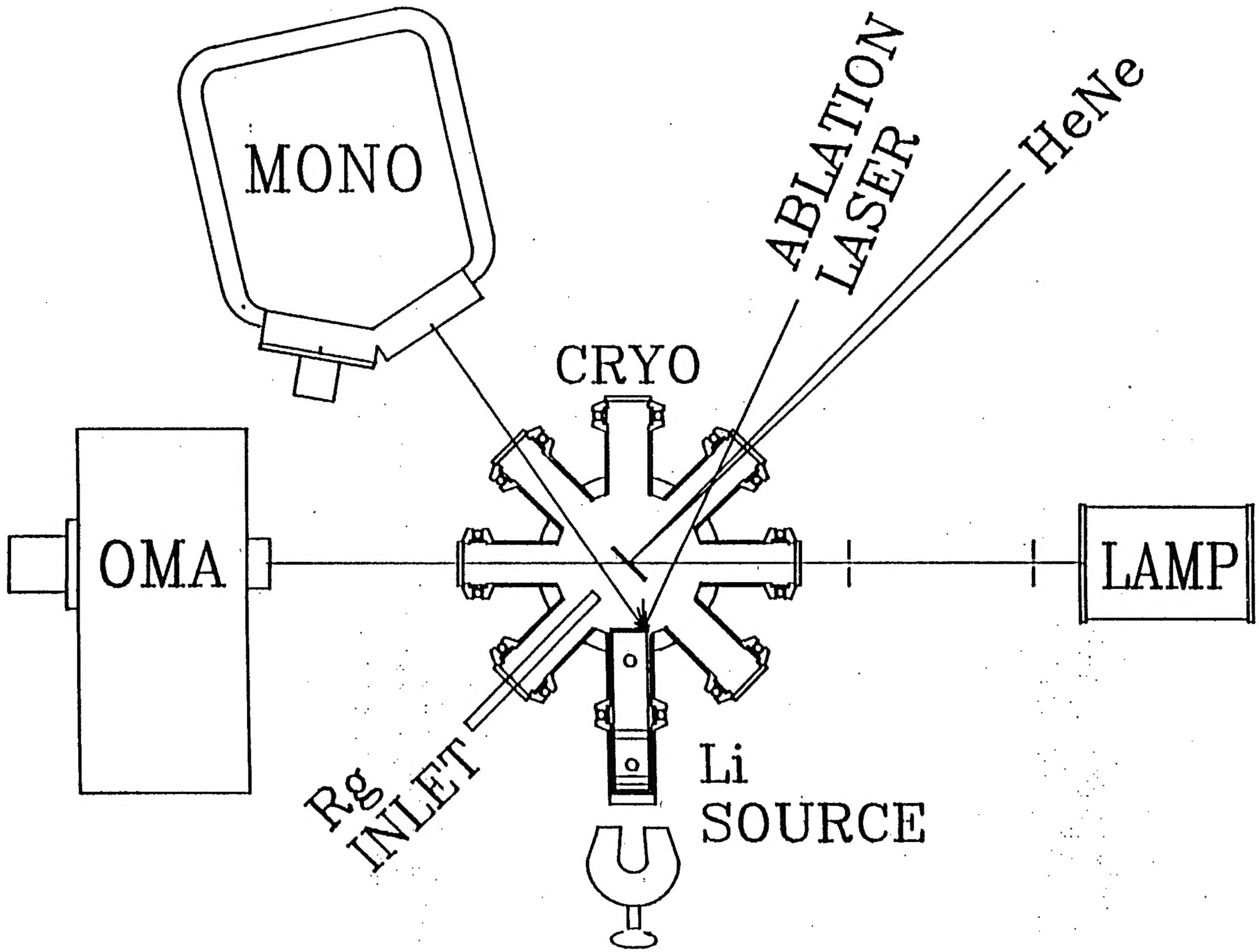
Greater Propellant Density

liquid H_2 @ 20 K : $\rho = 0.070$ g/cm^3

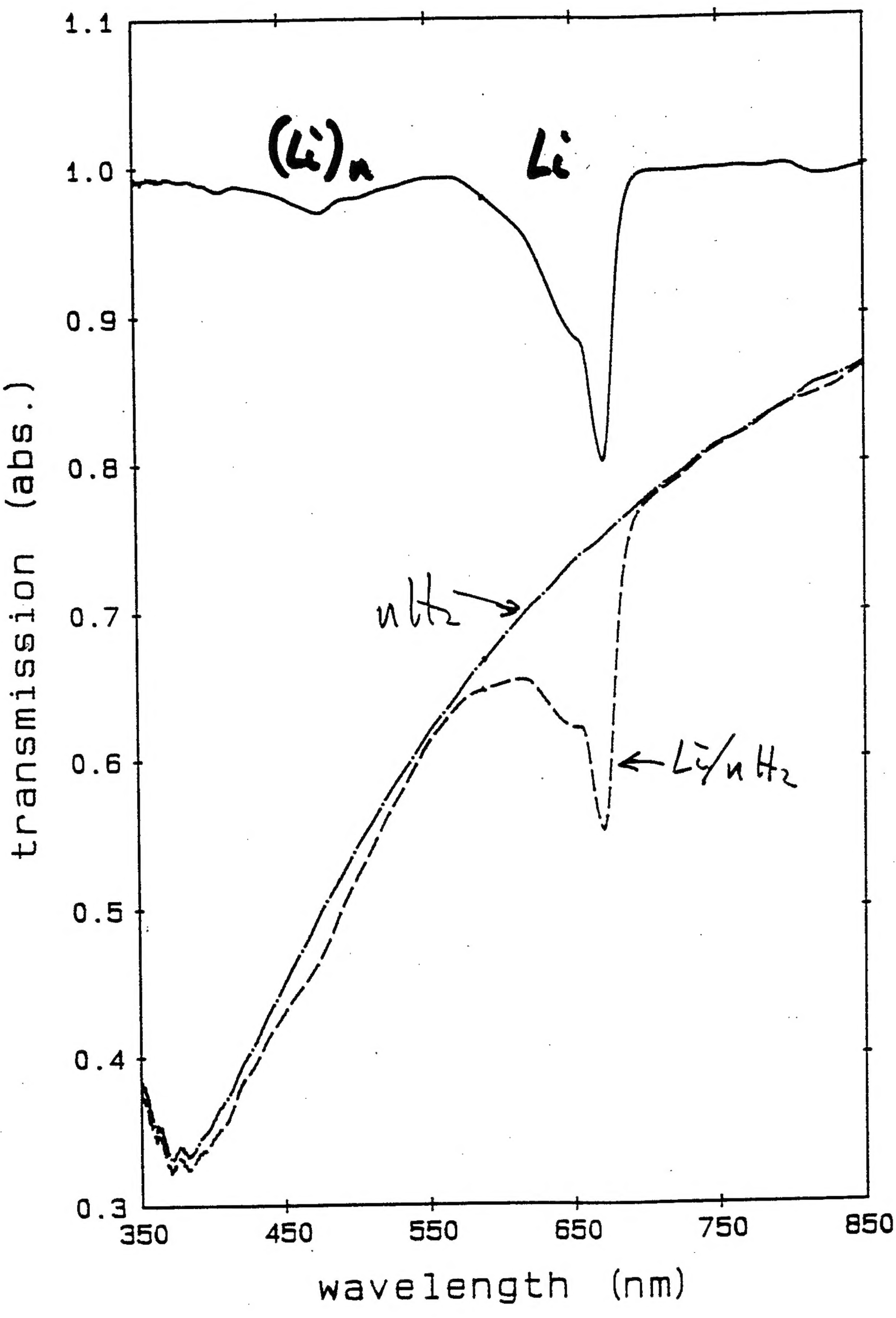
solid H_2 @ 2 K : $\rho = 0.087$ g/cm^3 (+25%)

50/50 liquid He/solid H_2 : $\rho = 0.105$ g/cm^3 (+50%)

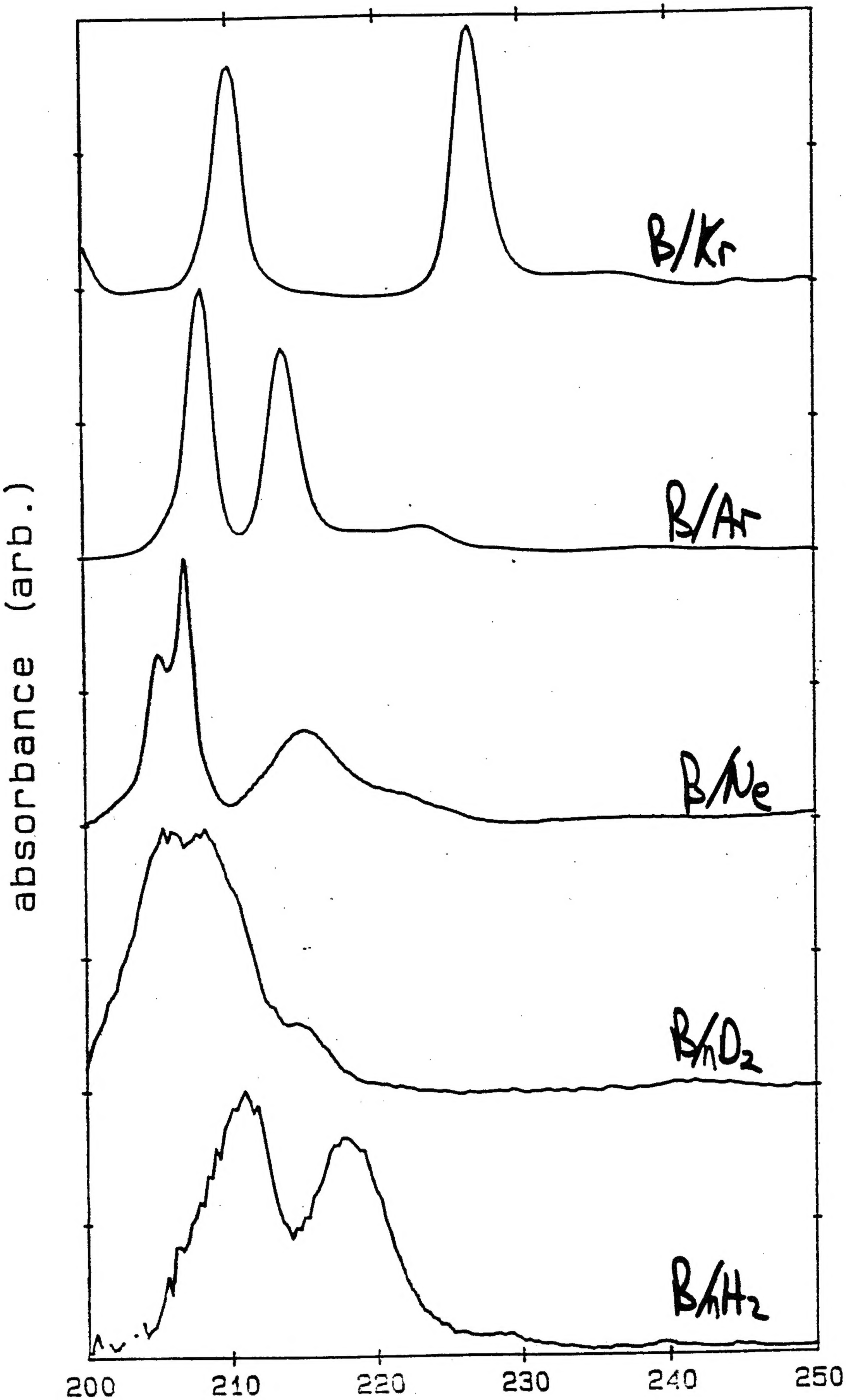
Experimental Diagram (c.1993)



Li/H_2 T=3K

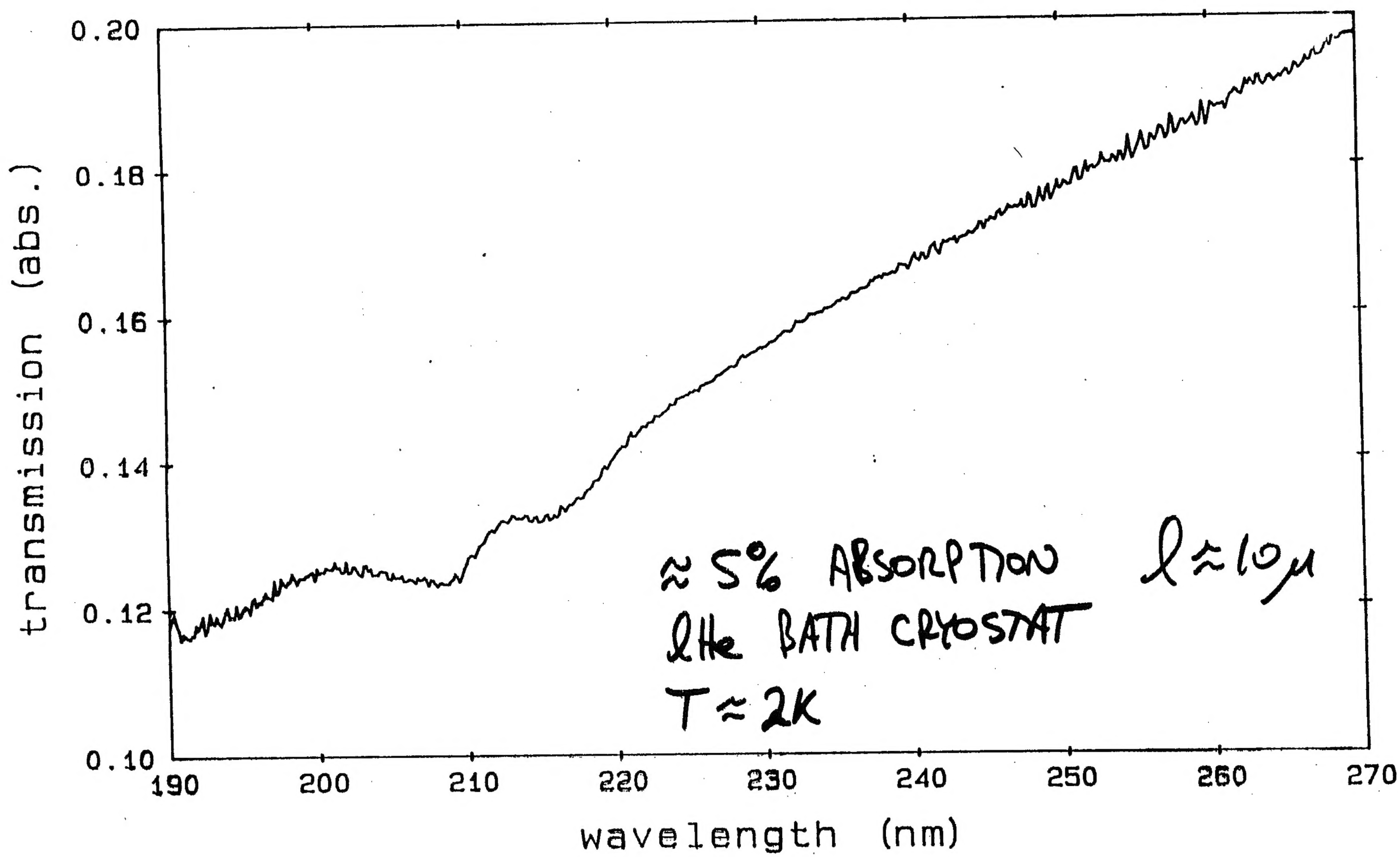


M.E. Fajardo, J. Chem. Phys. 98, 110 (1993).



S. TAM + M. E. FAJARDO, UNPUBLISHED.

B/n-H2 raw data (c1993)



Optical Scattering in Solid Hydrogen

Crystal Growing and Quality (p. 81)

"There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow."

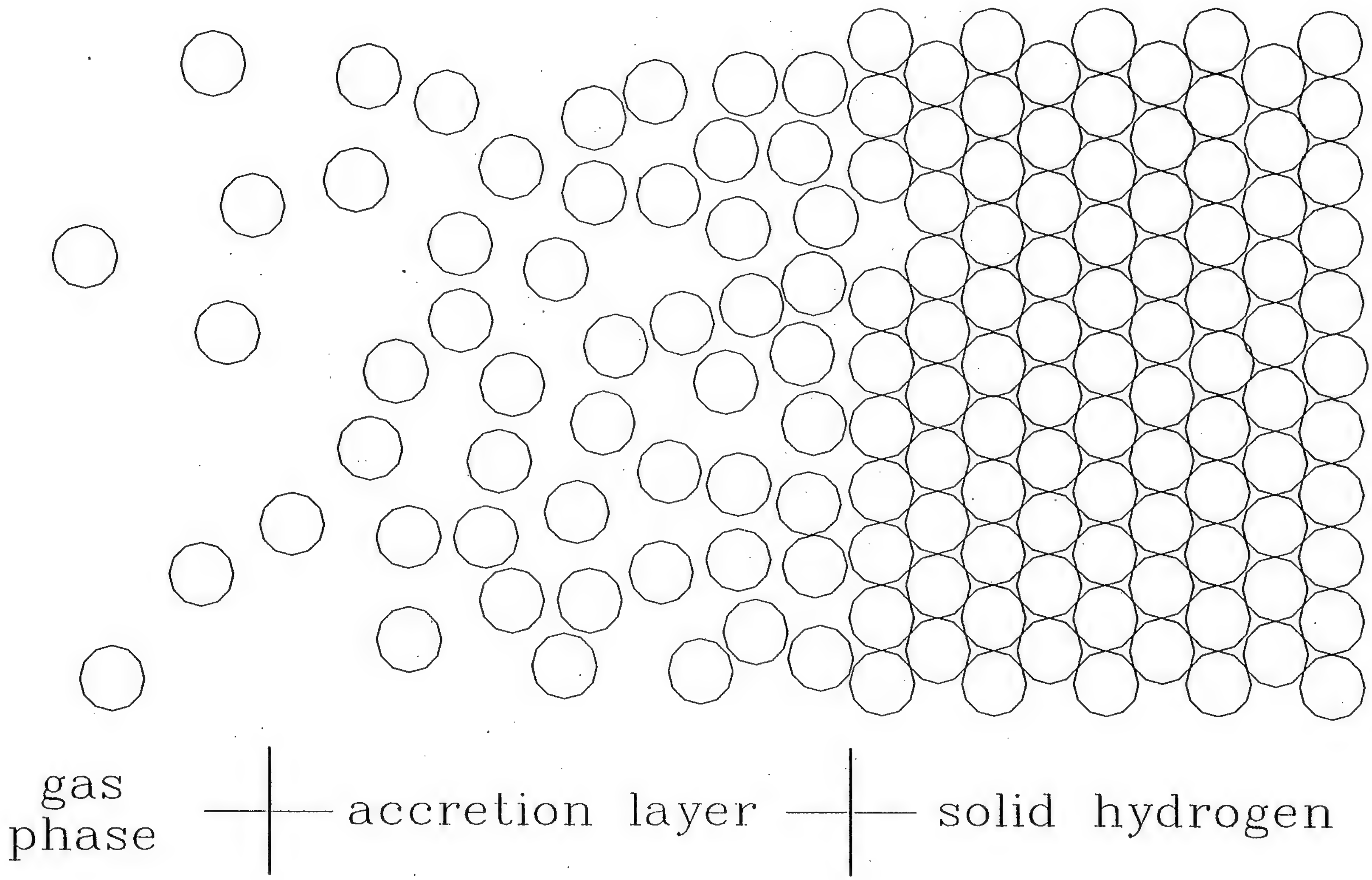
Crystallite Light Scattering (p. 83)

"The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!

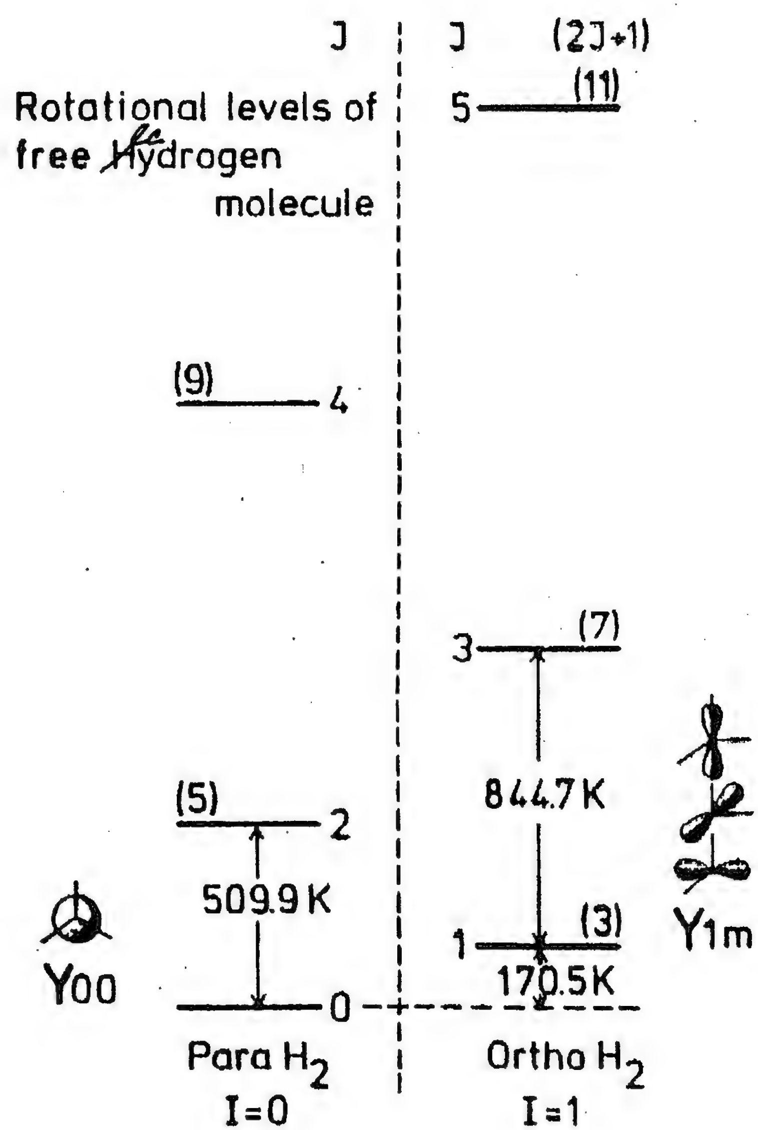
Yet a 1 mm-thick layer of hydrogen crystallites can be a completely opaque brown-black."

P.C. Souers,
<u>Hydrogen Properties for Fusion Energy</u>
(UC Press, Berkeley, 1986).

Deposition Cartoon



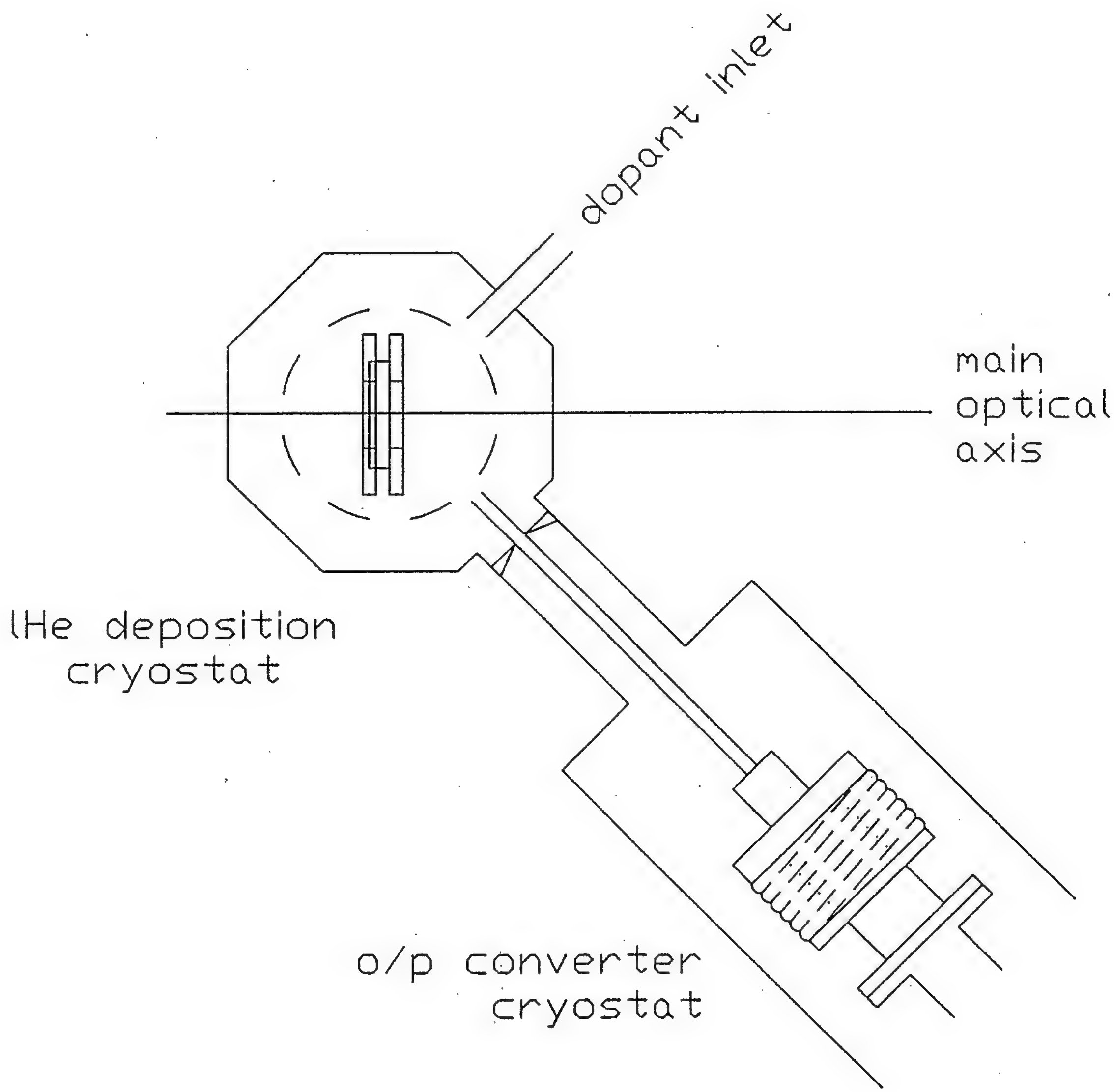
Ortho and Para Hydrogen



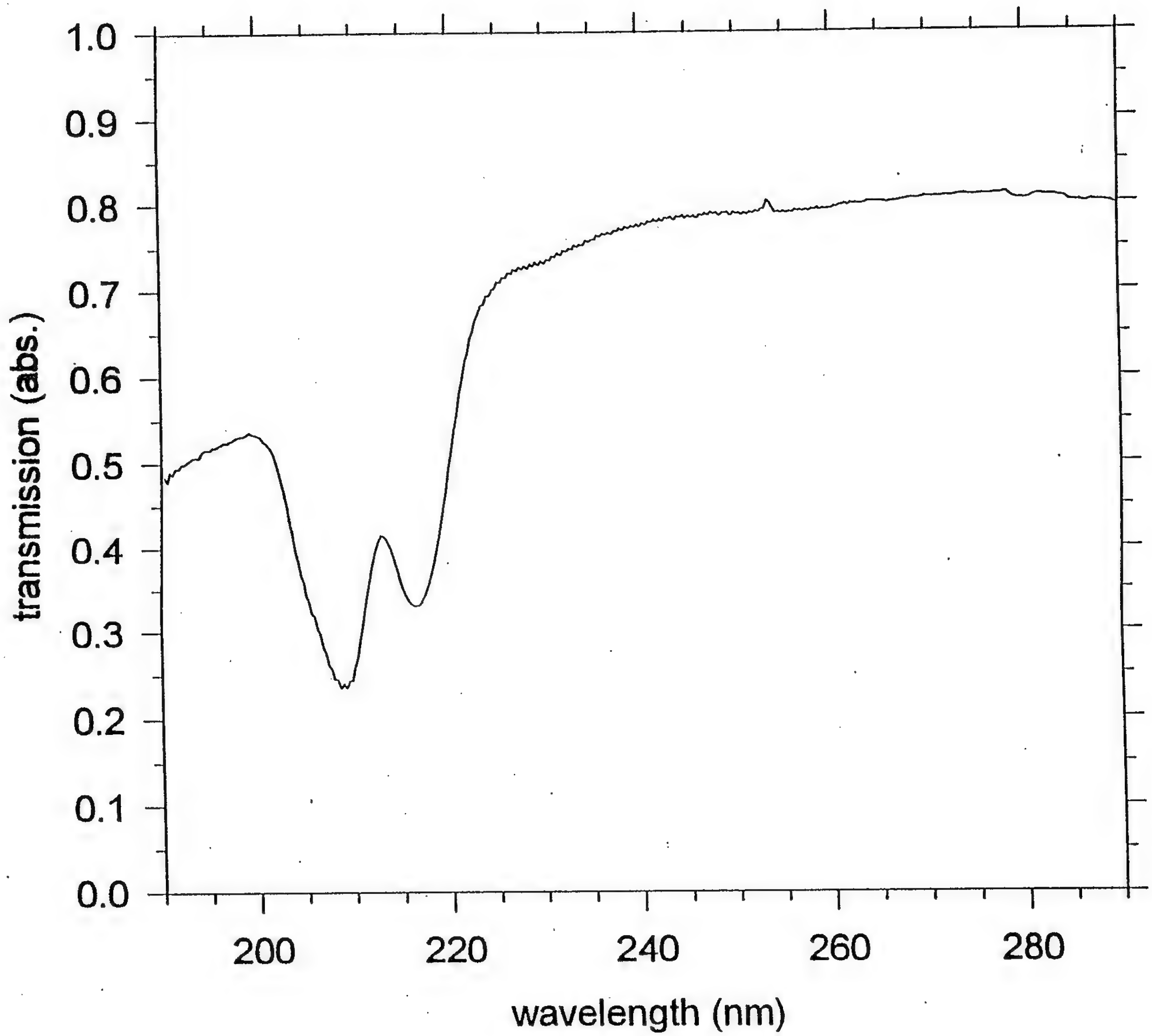
I.F. Silvera,
Rev. Mod. Phys. **52**, 393 (1980).

Experimental Diagram (c1997)

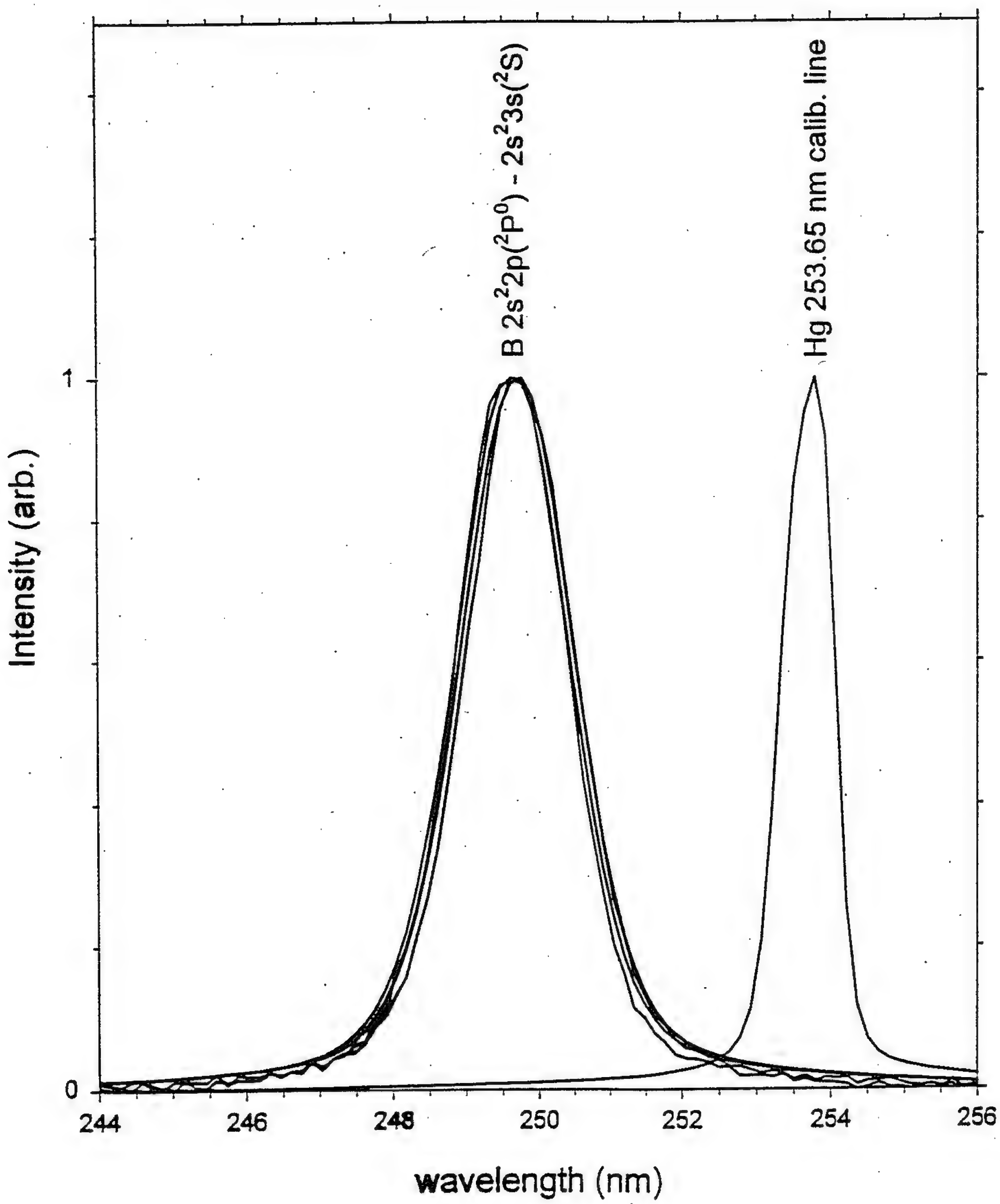
M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998)
S. Tam and M.E. Fajardo, Rev. Sci. Instrum. **70**, 1926 (1999)



UV Transmission of 1-mm Thick B/pH_2 Sample



B/pH_2 LIF
λ_{exc} = 207, 210, 217, and 220 nm



X

HEDM Cryosolid Propellants Status

~~PRIOR TO THIS EFFORT~~

* Demonstrated trapping of several energetic additives in solid hydrogen at concentrations below ~ 0.1%.

* Demonstrated gram-scale sample production method.

Outstanding Issues

* Increase energetic dopant concentrations above 1 %.

* Develop diagnostics for thick, concentrated samples.

AFRL/Edwards Experimental Approach

* Develop high-flux HEDM dopant sources.
    - materials compatibility with liquid B or Al
        - Bill Larson's poster
* Characterize gas-phase products of HEDM sources.
    - MPI/TOFMS
    - know species before & after deposition
        - Michelle DeRose's poster
* Develop IR absorption diagnostics.
    - dopant induced IR absorptions
        - Simon Tam's poster
    - high-resolution IR spectroscopy in solid pH_2
        - My poster and this talk

HEDM dopant recombination/reaction

* ideally:

$X + pH_2 \xrightarrow{T=2K} X/pH_2$	isolated atoms

* in practice:

$X + X + M \rightarrow X_2 + M$	recombination
$\rightarrow X_n$	
$X + H_2 + M \rightarrow HX + H + M$	reaction
$\rightarrow H_nX + M$	
$X_n + H_2 + M \rightarrow HX_n + H + M$	both
$\rightarrow H_mX_n + M$	

The Perils of Calorimetry

A.M. Bass and H.P. Broida, "Formation and Trapping of Free Radicals" (Academic, New York, 1960).

TABLE IX

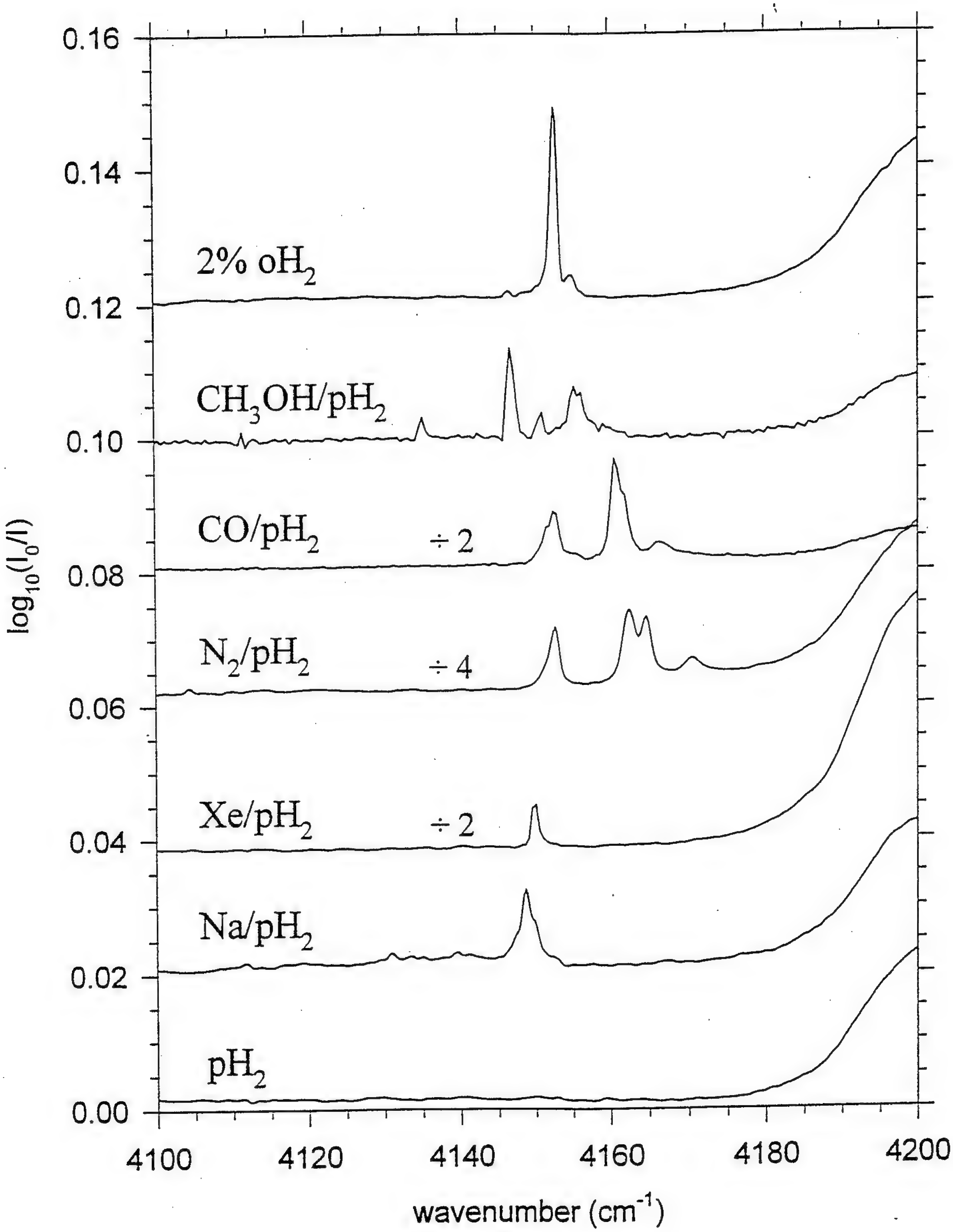
CONCENTRATIONS OF FREE RADICALS REPORTED

Radical	Matrix	Mole per cent radicals	Method of production and estimate[a]	Reference
O	O_2	4–20	Gas, cal	Minkoff *et al.* (1959).
		<3	Gas, IR	Harvey and Bass (1958)
		~1	Gas, cal	Broida and Lutes (1956)
OH	$Ca(OH)_2$	0.6	γ, ESR	R. Livingston[b]
N	N_2	4	Gas, cal	Minkoff *et al.* (1959)
		0.2	Gas, cal	Broida and Lutes (1956)
		0.03	γ, ESR	Wall *et al.* (1959b)
		>0.03	Gas, cal	Fontana (1958)
		0.01–0.04	Gas, MS	Fontana[c]
OH(?)	HCOOH	0.2	γ, ESR	Matheson and Smaller (1955)
CH_3	CH_4	0.14	γ, ESR	Wall *et al.* (1959a)
H	CH_4	0.1	γ, ESR	Wall *et al.* (1959a)
N	NH_3	0.1	Gas, ESR	Cole and Harding (1958)
H	$HClO_4—H_2O$	0.1	γ, ESR	Livingston *et al.* (1955)
H	H_2O	0.01	γ, ESR	Matheson and Smaller (1955)
H, NH_2(?)	NH_3	0.01	γ, ESR	Matheson and Smaller (1955)
$\dot{R}OH$	Alcohols	~0.01	UV, ESR	D. Ingram[b]
H	H_2	0.0006	γ, ESR	Wall *et al.* (1959a)

[a] Abbreviations: gas = rapid condensation of gaseous radicals; γ = gamma ray *in situ* production; UV = photolytic *in situ* production; IR = infrared analysis; cal = calorimetry; MS = magnetic susceptibility.

[b] Private communication.

[c] Fontana, B. J. (1959). *J. Chem. Phys.* **31**, 148.



0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
log10(I0/I)
2% oH2
CH3OH/pH2
CO/pH2
÷ 2
N2/pH2
÷ 4
Xe/pH2
÷ 2
Na/pH2
pH2
4100
4120
4140
4160
4180
4200
wavenumber (cm-1)

High Resolution IR Spectroscopy in Solid pH_2

T. Momose, K.E. Kerr, D.P. Weliky, C.M. Gabrys, R.M. Dickson and T. Oka,
J. Chem. Phys. **100**, 7840 (1994).

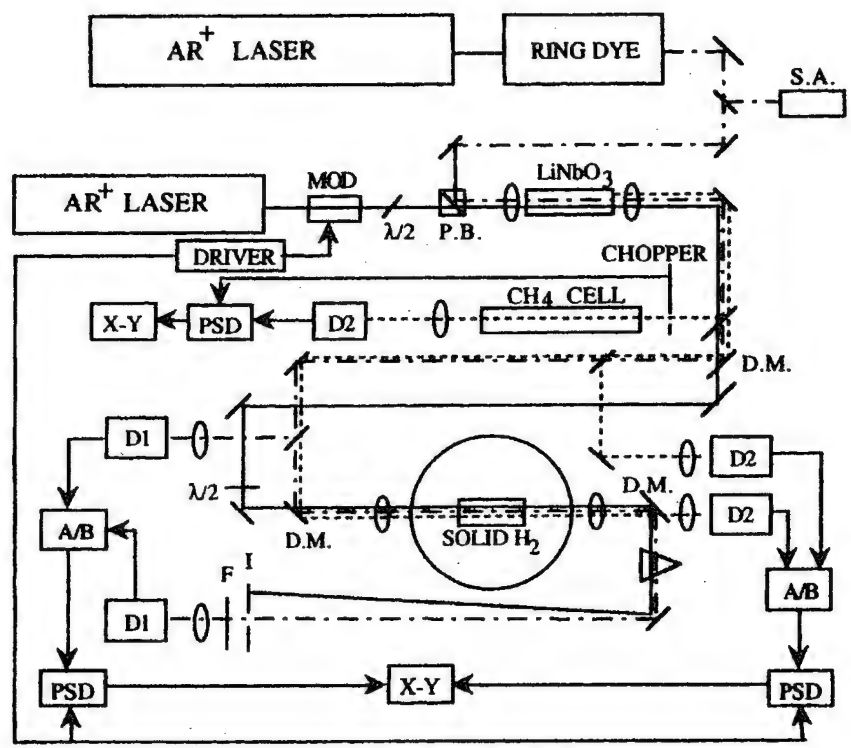
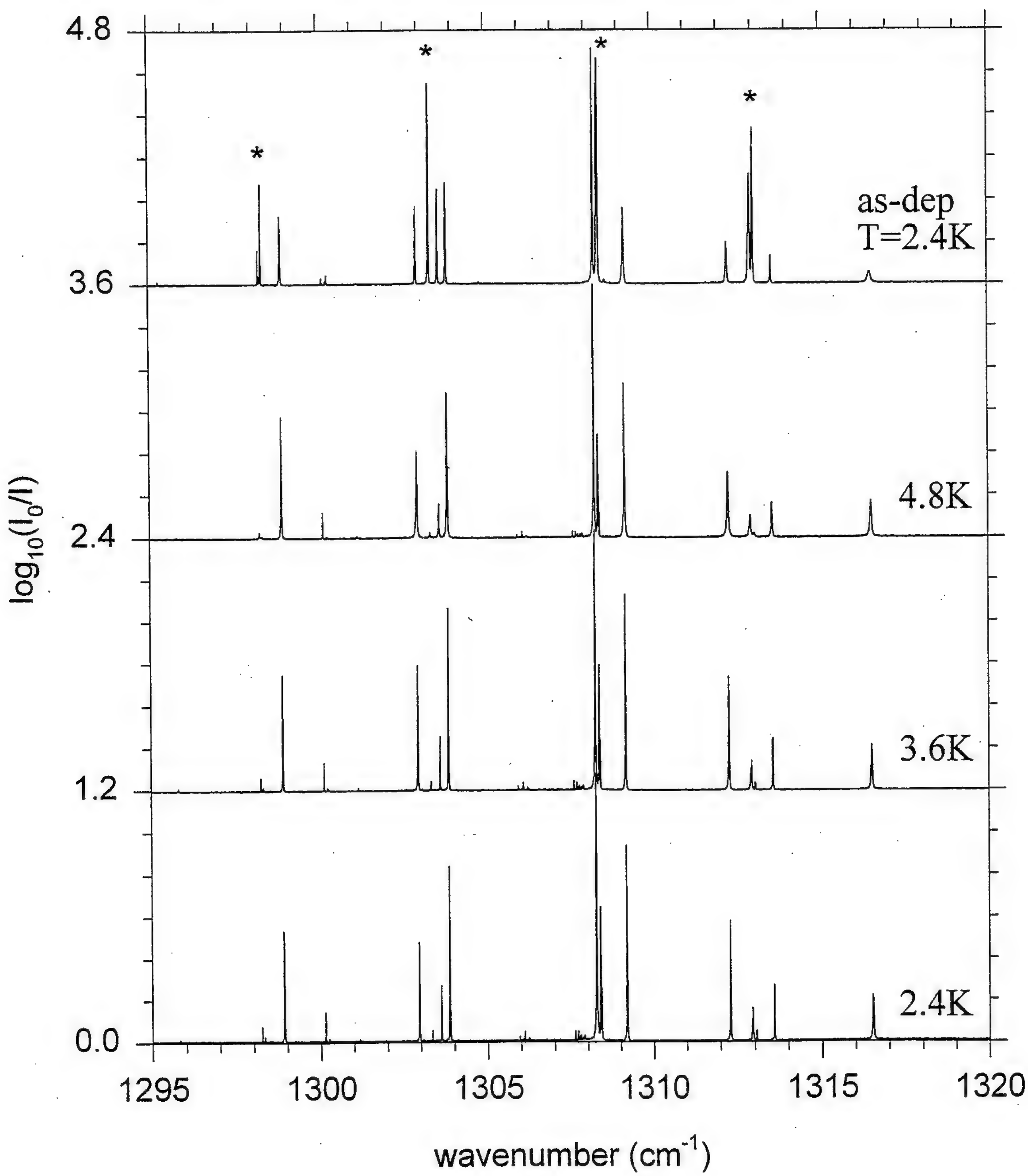
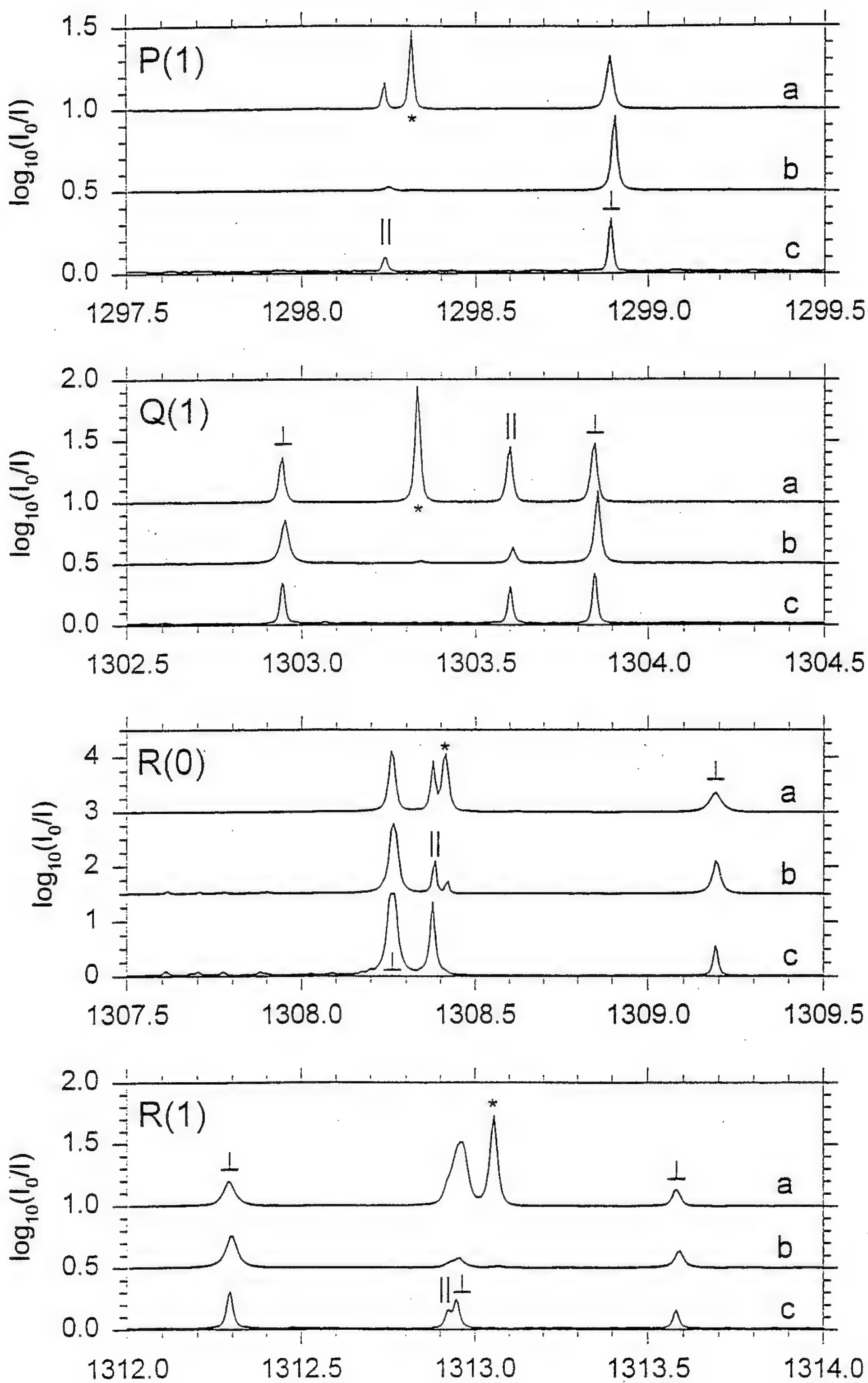


FIG. 1. Apparatus for the simultaneous spectroscopy of the infrared and Raman transitions. The nonlinearity of $LiNbO_3$ is used for the former and that of solid H_2 is used for the latter. D.M., dichroic mirror; S. A., spectrum analyzer; P. B., polarizer beamsplitter.

ν_4 CH_4/pH_2 absorptions

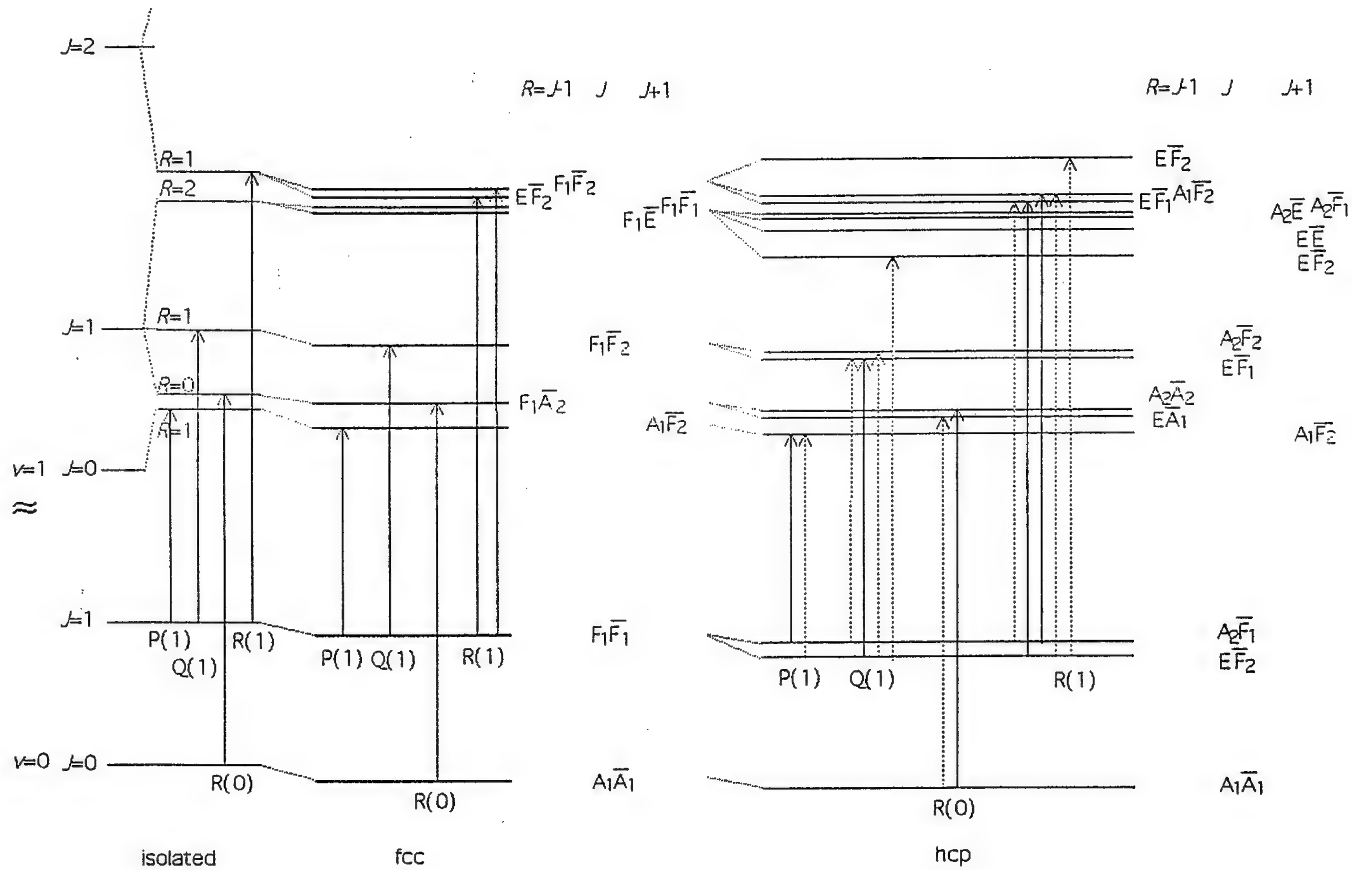


ν_4 CH_4/pH_2 Absorptions



CH_4/pH_2 Energy Levels

S. Tam, M.E. Fajardo, H. Katsuki, H. Hoshina, T. Wakabashi, and T. Momose, J. Chem. Phys., submitted.



HEDM Cryosolids Accomplishments

(a list of "things that'll never work.")

* Trapped Li, B, Na, Mg, Al atoms in solid hydrogen.
* Demonstrated production of gram-scale transparent pH_2 solids by rapid vapor deposition.
* Demonstrated that vapor deposited pH_2 solids are densest close-packed solids, NOT amorphous.
* Generalized phenomenon of dopant induced IR activity in pH_2 host; diagnostic for thick, concentrated samples.

Future Directions

* Develop high-flux HEDM dopant sources.

* Characterize gas-phase products of HEDM sources.

* Develop IR absorption diagnostics.
  - dopant induced IR absorptions
  - high-resolution IR spectroscopy in solid pH_2

National Research Council (1998)

Report: “Maintaining U.S. Leadership in Aeronautics -- Breakthrough Technologies to Meet Future Air and Space Transportation Needs and Goals”

Assessment:

“Steady progress has been made in research on cryogenic solid propellants. Laboratory experiments have demonstrated the feasibility of ingredient storage, albeit at low concentrations, and small thruster experiments have demonstrated the stable combustion of pure cryo-solid propellants in a hybrid configuration. Much more research will be necessary before this can be called a breakthrough technology and before its readiness for transition into real launch systems can be demonstrated. Research areas are listed below:”

National Research Council (1998)

Report: "Maintaining U.S. Leadership in Aeronautics -- Breakthrough Technologies to Meet Future Air and Space Transportation Needs and Goals"

Recommended Future Research Areas:

* computational studies of the dynamics, thermodynamics, and spectroscopy of energetic additives to cryogenic solids
* spectroscopic characterization of highly energetic species trapped in energetic matrices at concentrations of at least 1 percent
* production methods for energetic species
* scale-up production of cryogenic solid propellants with energetic species concentrations of at least 1 percent
* methods of transporting and combusting doped cryogenic solids"